



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 449 453 A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91302130.9**

(51) Int. Cl.⁵: **C07C 2/08, C07C 2/24,
C07C 2/22**

(22) Date of filing: **13.03.91**

(30) Priority: **28.03.90 US 500631
14.05.90 US 522941
21.05.90 US 525807
30.04.90 US 516931
04.09.90 US 577385
30.04.90 US 516870**

(43) Date of publication of application:
02.10.91 Bulletin 91/40

(84) Designated Contracting States:
BE DE FR GB IT

(71) Applicant: **TEXACO CHEMICAL COMPANY**
3040 Post Oak Boulevard
Houston, Texas 77056(US)

(72) Inventor: **Marquis, Edward Thomas**
9004 Colinfield Drive
Austin, Texas 78758(US)
Inventor: **Sanderson, John Ronald**
P O Box 587
Leander, Texas 78641(US)
Inventor: **Knifton, John Frederick**
P O Box 15730
Austin, Texas 78726(US)

(74) Representative: **Brock, Peter William et al**
URQUHART-DYKES & LORD 91 Wimpole
Street
London W1M 8AH(GB)

(54) **Process for oligomerizing olefins to prepare base stocks for synthetic lubricants.**

(57) Linear olefins having 10 to 24 carbon atoms can be oligomerized to form synthetic lubricant base stocks by means of acidic calcium montmorillonite clay having a moisture content up to 20 wt%, a residual acidity of up to 30 mg KOH/g, and a surface area of 300 M²/g or greater. In a preferred embodiment, a Lewis acid such as aluminium nitrate is deposited on the clay.

The linear olefins can be alpha olefins, internal olefins or mixtures thereof, or the linear olefins can be co-oligomerized with propylene, with 1,3-diisopropenylbenzene or alpha-methylstyrene, or with vinylidene olefins.

The oligomers are preferably hydrogenated to improve their stability.

EP 0 449 453 A2

The invention relates to the preparation of synthetic lubricant base stocks, and more particularly to synthetic lubricant base stocks made by oligomerizing compositions comprising linear olefins by means of certain acidic montmorillonite clay catalysts.

Synthetic lubricants are prepared from man-made base stocks having uniform molecular structures, and consequently having well-defined properties that can be tailored to specific applications. Mineral oil base stocks, on the other hand, are prepared from crude oil and are complex mixtures of naturally occurring hydrocarbons. The greater uniformity of synthetic lubricants generally results in superior performance properties. For example, synthetic lubricants have excellent thermal stability. As automobile engines are reduced in size to save weight and fuel, they run at higher temperatures, and therefore require a more thermally-stable oil. Because lubricants made from synthetic base stocks have such properties as excellent oxidative/thermal stability, very low volatility, and good viscosity indices over a wide range of temperatures, they offer better lubrication and permit longer drain intervals, with less oil vaporization loss between oil changes.

Synthetic base stocks may be prepared by oligomerizing internal and alpha-olefin monomers to form a mixture of dimers, trimers, tetramers, and pentamers, with minimal amounts of higher oligomers. The unsaturated oligomer products are then hydrogenated to improve their oxidative stability. The resulting synthetic base stocks have uniform isoparaffinic hydrocarbon structures similar to high quality paraffinic mineral base stocks, but have the superior properties mentioned, due to their greater uniformity.

Synthetic base stocks are produced in a broad range of viscosity grades. It is common practice to classify the base stocks by their viscosities, measured in centistokes (cSt) at 100°C. Those base stocks with viscosities less than or equal to 4 cSt are commonly referred to as "low viscosity" base stocks, whereas base stocks having a viscosity in the range from 40 to 100 cSt are commonly referred to as "high viscosity" base stocks. Base stocks having a viscosity of 4 to 8 cSt are referred to as "medium viscosity" base stocks. Low viscosity base stocks generally are recommended for low temperature applications. Applications at higher temperatures, such as in motor oils, automatic transmission fluids, turbine lubricants, and other industrial lubricants, generally require higher viscosities, such as those provided by medium viscosity base stocks (i.e. 4 to 8 cSt grades). High viscosity base stocks are used in gear oils and as blending stocks.

The viscosity of the base stocks is determined by the length of the oligomer molecules formed during the oligomerization reaction. The degree of oligomerization is affected by the catalyst and reaction conditions employed during the oligomerization reaction. The length of the carbon chain of the monomer starting material also has a direct influence on the properties of the oligomer products. Fluids prepared from short-chain monomers tend to have low pour points and moderately low viscosity indices, whereas fluids prepared from long-chain monomers tend to have moderately low pour points and higher viscosity indices. Oligomers prepared from long-chain monomers generally are more suitable than those prepared from shorter-chain monomers for use as medium viscosity synthetic lubricant base stocks.

One known approach to oligomerizing long-chain olefins to prepare synthetic lubricant base stocks, is to contact the olefin with boron trifluoride, together with a promotor, at a reaction temperature sufficient to effect oligomerization of the olefin; See, for example, US-A-4400565, -4420646, -4420647 and -4434308 and EP-A-0136377. Boron trifluoride gas (BF₃) is a pulmonary irritant, however, and breathing the gas, or fumes formed by hydration of the gas with atmospheric moisture, poses hazards preferably avoided. Moreover, the disposal/neutralization of BF₃ raises environmental concerns. Thus, a method for oligomerizing long-chain olefins using a non-hazardous, non-polluting catalyst would be a substantial improvement in the art.

Kuliev et al. attempted to prepare synthetic lubricants by oligomerizing long-chain (C₉-C₁₄) olefins using non-hazardous and non-polluting acidic clays, comprising sulphuric acid - and hydrochloric acid-activated bentonites from the Azerbaidzhan SSR; see Kuliev, Abasova, Gasanova, Kotlyarevskaya, and Valiev, "Preparation of High-Viscosity Synthetic Lubricants Using an Aluminosilicate Catalyst," Institute of Petrochemical Processes of the Academy of Sciences of the Azerbaidzhan SSR, Azer. Neft. Khoz., 1983, No. 4, pages 40-43. Kuliev et al. concluded, however, that "it was not possible to prepare viscous or high-viscosity oils by olefin polymerization over an aluminosilicate catalyst" and that "hydrogen redistribution reactions predominate with formation of aromatic hydrocarbon, coke, and paraffinic hydrocarbon." US-A-453 1014 discloses the use of Wyoming bentonite to oligomerize shorter-chain olefins, but this process does not make it possible to obtain a product high in dimer, trimer and tetramer, and low in disproportionation products.

We have surprisingly discovered that it is possible to prepare synthetic lubricant base stocks in good yield by oligomerizing long-chain olefins using certain acidic montmorillonite clay catalysts. We have found that a high conversion of long-chain olefin to dimer, trimer, and tetramer may be obtained, with formation of very little concomitant hydrogen redistribution by-product, by using certain acidic calcium montmorillonite

clays.

One embodiment of this invention relates to a process for the preparation of oligomers or co-oligomers of linear olefins containing from 10 to 24 carbon atoms in which an olefin composition comprising said olefins is contacted with a catalyst. The catalyst is an acidic calcium montmorillonite clay having a moisture
5 content up to 20 wt.%, a residual acidity of up to 30 mg KOH/g, and a surface area of 300 M²/g or greater.

The linear olefins may comprise alpha-olefins, internal olefins, or a mixture thereof. Optionally, the linear olefins may be employed in admixture with up to 20 weight % of propylene, or of 1,3-diisopropenyl benzene or alpha-methylstyrene. They may also be employed in admixture with vinylidene olefins having 10 to 24 carbon atoms, eg. in amount of 5 to 40 weight %.

10 In a preferred embodiment, at least 0.01 wt% of a Lewis Acid selected from aluminium nitrate, zinc chloride, and nickel chloride may be deposited on the day.

According to another preferred embodiment, the oligomerized product is hydrogenated.

The olefin monomer feed stocks used in the present invention may be selected from (1) alpha-olefins having the formula $R''CH=CH_2$, where R'' is alkyl having 8 to 22 carbon atoms, and (2) internal olefins
15 having the formula $RCH=CHR'$, where R and R' are the same or different alkyl having 1 to 20 carbon atoms, provided that the total number of carbon atoms in any one olefin is from 10 to 24, inclusive. A preferred range for the total number of carbon atoms in any one olefin molecule is 12 to 18, inclusive, with an especially preferred range being 13 to 16, inclusive. Mixtures of internal and alpha-olefins may be used, as well as mixtures of olefins having different numbers of carbon atoms, provided that the total number of
20 carbon atoms in any one olefin is from 10 to 24, inclusive. The alpha and internal-olefins to be oligomerized in this invention may be obtained by processes well-known to those skilled in the art and are commercially available.

According to one embodiment of the invention, it has been discovered that certain properties of these synthetic lubricant base stocks are improved when the olefin feed comprises a mixture of alpha and
25 internal-olefin having up to 50 wt.% of internal-olefin. When oligomers produced in this manner are hydrogenated, they yield synthetic lubricant base stocks having higher viscosity indices. A higher viscosity index indicates that the synthetic lubricant will be less susceptible to a change in viscosity when subjected to a change in temperature. This is a desirable characteristic for most lubricating applications. In addition, these synthetic lubricants have a lower pour point, another desirable feature.

30 The oligomerization reaction may be carried out in either a stirred slurry reactor or in a fixed bed continuous flow reactor. In a continuous reaction, up to 50 wt.% of the olefin feed may be made to comprise internal-olefin by either or both of two methods. According to the first method, separate feedstreams of internal and alpha-olefins may be mixed in the desired weight ratio before or upon entering the reactor containing the clay catalyst bed. Alternatively, or in addition, the second method provides that
35 internal olefin may be introduced to the catalyst bed in a recycle stream. When alpha-olefin in the feedstream passes through the clay catalyst in the reactor, a portion of the olefin remains un-oligomerized. Most of the olefin remaining in monomer form will have isomerized to internal olefin. Thus, the product of the oligomerization reaction has three components: oligomer; internal-olefin monomer; and alpha-olefin monomer. The alpha and internal-olefins may be stripped from the oligomer and recycled to the catalyst
40 bed for oligomerization. The monomer stripping step should be conducted under mild conditions. Distillation at temperatures exceeding 210°C may cause the oligomers to break down in some fashion and come off as volatiles. Preferably, therefore, the reboiler or pot temperature should be kept at or under 180°C when stripping out the monomer. Procedures known by those skilled in the art to be alternatives to fractional distillation also may be employed to separate the monomers from oligomers.

45 In summary, internal olefin may be introduced to the catalyst bed directly as a feedstream component and/or as a recycled isomer of the alpha-olefin feed. Additionally, when internal-olefin is introduced as a feedstream component, any un-oligomerized internal-olefin also may be recycled to the catalyst bed. When either or both methods are employed, no more than 50 wt.% of the olefin present in the catalyst bed at any one time should comprise internal-olefin.

50 In a batch reaction system, internal-olefin should comprise up to 50 wt.% of the olefin starting material. The internal-olefin component may be obtained by processes known to those skilled in the art, purchased commercially, and/or may be distilled from the product of a prior oligomerization reaction and recycled by inclusion in a subsequent batch oligomerization reaction.

According to another embodiment, it has surprisingly been found that synthetic lubricant base stocks
55 with a lower pour point and an improved viscosity index may be obtained when the oligomers are prepared by co-oligomerizing a mixture of up to 20 wt.% as propylene and more than 80 wt.% of the C₁₀-C₂₄ olefin, preferably alpha-olefin, in the presence of the clay catalysts. Moreover, incorporating the propylene lowers the cost of producing the base stocks, by replacing a portion of the more expensive long-chain olefin feed

with propylene.

Preferably, the mixture of C₁₀-C₂₄ olefin and propylene contains from 2 to 10 wt.% of propylene. When oligomers produced in this manner are hydrogenated, they yield synthetic lubricant base stocks having a lower pour point. Additionally, when the propylene comprises no more than 15 wt. % of the C₁₀-C₂₄ olefin/propylene mixture, the resulting synthetic lubricants have a higher viscosity index.

According to a further embodiment of the invention, synthetic lubricant base stocks with a lower pour point and a higher viscosity may be obtained when the oligomers are prepared by co-oligomerizing a mixture of up to 20 wt.% of 1,3-di-isopropenyl benzene or alpha-methylstyrene and more than 80 wt.% of C₁₀-C₂₄ olefin, preferably alpha-olefin, in the presence of the clay catalysts.

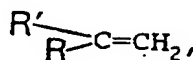
Preferably, the mixture of C₁₀-C₂₄ olefin and 1,3-di-isopropenyl benzene or alpha-methylstyrene contains from 5 to 15 wt.% of 1,3-di-isopropenyl benzene or alpha-methylstyrene. It is most preferred that the mixture contains about 10 wt.% of 1,3-di-isopropenyl benzene or alpha-methylstyrene. When oligomers produced in this manner are hydrogenated, they yield synthetic lubricant base stocks having a lower pour point.

Additionally, when the 1,3-di-isopropenyl benzene comprises more than 5 wt.% of the C₁₀-C₂₄ olefin/1,3-di-isopropenyl benzene mixture, the resulting synthetic lubricants have a higher viscosity.

According to a further embodiment, it is possible to use the clay catalysts for co-oligomerizing a mixture of (1) a long-chain (C₁₀-C₂₄) vinylidene olefin and (2) the above-mentioned straight chain C₁₀-C₂₄ alpha-olefins and/or internal-olefins. US-A-4214111 discloses co-polymerizing higher alpha-olefins with a vinylidene olefin, but, the vinylidene olefin is a shorter-chain olefin, (isobutylene or di-isobutylene), and the catalyst employed is an aluminium halide catalyst, which may be corrosive. The process according to the present invention achieves a high conversion of olefin to oligomers incorporating higher molecular weight vinylidenes using a more easily handled catalyst.

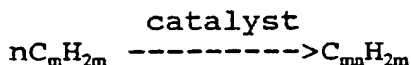
It has been further discovered that the pour point of the synthetic lubricant base stocks is improved when the olefin feed comprises a mixture of C₁₀-C₂₄ vinylidene olefin and C₁₀-C₂₄ alpha- and/or internal-olefin. Preferably, from 5 to 40 wt.% of the mixture of starting materials comprises vinylidene olefin. More preferably, from 15 to 30 wt.% of the mixture of starting materials comprises vinylidene olefin. It is especially preferred that about 20 wt.% of the starting materials is vinylidene olefin.

The vinylidene olefins have the formula

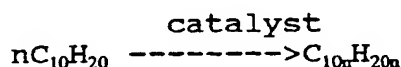


where R and R' are the same or different alkyl radicals of 1 to 21 carbon atoms, provided that (as with the straight chain olefins) the total number of carbon atoms in any one olefin is from 10 to 24, inclusive, preferably 14 to 18, and more preferably 14 to 16 carbon atoms. Mixtures containing the vinylidene olefins and both internal- and alpha- olefins may be used, as well as mixtures containing vinylidene olefins and either internal- or alpha-olefins. The greatest improvement in pour point, over base stocks prepared without the inclusion of vinylidene olefin, is observed when base stocks prepared from alpha-olefins alone are compared with base stocks prepared from mixtures which include vinylidene olefins. Only a small improvement is observed over base stocks which include a substantial percentage of internal olefin.

The oligomerization reaction may be represented by the following general equation:



where n represents moles of monomer and m represents the number of carbon atoms in the monomer. Thus, the oligomerization of 1-decene may be represented as follows:

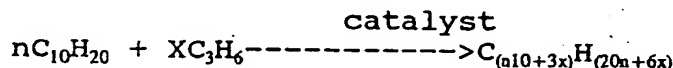


The co-oligomerization of straight chain with vinylidene olefins will follow a corresponding course.

The reaction occurs sequentially. Initially, olefin monomer reacts with olefin monomer to form dimers. The dimers that are formed then react with additional olefin monomer to form trimers, and so on. This

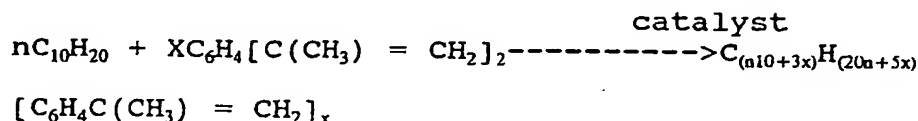
results in an oligomer product distribution that varies with reaction time. As the reaction time increases, the olefin monomer conversion increases, and the selectivities for the heavier oligomers increase. Generally, each resulting oligomer contains one double bond.

Similarly, co-oligomerization of propylene and 1-decene may be represented as follows:



where n represents moles of C_{10} - C_{24} olefin and x represents moles of propylene.

The co-oligomerization of 1,3-di-isopropenyl benzene and a C_{10} - C_{24} olefin, such as 1-decene, may result in several reactions. For example, one propenyl group of the 1,3-di-isopropenyl benzene may react with decene, as represented by the following equation:

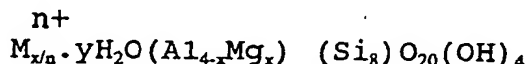


where n represents moles of C_{10} - C_{24} olefin and x represents moles of 1,3-di-isopropenyl benzene. Additionally, both propenyl groups may react with decene. One or both propenyl groups also may react with other 1,3-di-isopropenyl benzene molecules. Finally, 1,3-di-isopropenyl benzene is a reactive aromatic, and may undergo aromatic substitution. The substituted aromatic may then react with decene or 1,3-di-isopropenyl benzene.

A similar course is followed when alpha-methylstyrene is co-oligomerized with the C_{10} - C_{24} olefin.

The catalysts used to effect the oligomerization reaction according to invention are certain silica-alumina clays, also called aluminosilicates. Silica-alumina clays primarily are composed of silicon, aluminium, and oxygen, with minor amounts of magnesium and iron in some instances. Variations in the ratios of these constituents, and in their crystal lattice configurations, result in some fifty separate clays, each with its own characteristic properties.

Smectite clays are one class of silica-alumina clays. Smectite clays have a small particle size and unusual intercalation properties which afford them a high surface area. Smectites comprise layered sheets of octahedral sites between sheets of tetrahedral sites, where the distance between the layers can be adjusted by swelling, using an appropriate solvent. Three-layered sheet-type smectites include montmorillonites. The montmorillonite structure may be represented by the following formula:



where M represents the interlamellar (balancing) cations, normally sodium or lithium; and x, y and n are numbers.

Montmorillonite clays may be acid-activated by such mineral acids as sulphuric acid and hydrochloric acid. Mineral acids activate montmorillonites by attacking and solubilizing structural cations in the octahedral layers. This opens up the clay structure and increases surface area. These acid-treated clays act as strong Bronsted acids. We have discovered that certain acid-treated montmorillonite clay catalysts are particularly effective for preparing synthetic lubricant base stocks in good yield by oligomerizing long-chain olefins. These clays are acidic calcium montmorillonite clays having a moisture content up to 20 wt.%, a residual acidity from 3 to 30 mg KOH/g (when titrated to a phenolphthalein end point), and a surface area of 300 M^2/g or more. Illustrative examples include Filtrol grade 24, having a moisture content of 12 wt.%, a residual acidity of 8.5 mg KOH/g, and a surface area of 425 M^2/g ; Filtrol grade 124, having a moisture content of 2 wt.%, a residual acidity of 7.0 mg KOH/g, and a surface area of 400 M^2/g ; Filtrol grade 13, having a moisture content of 16 wt.%, a residual acidity of 15 mg KOH/g, and a surface area of 300 M^2/g ; Filtrol grade 113, having a moisture content of 4 wt.%, a residual acidity of 10 mg KOH/g, and a surface area of 300 M^2/g ; and Filtrol grade 224, having virtually no moisture, and having a residual acidity of 3.0 mg KOH/g, and a surface area of 350 M^2/g .

Preferably, the catalyst is activated by heat treatment before carrying out the oligomerization reaction.

We have found that heat treatment of the catalyst before the oligomerization reaction causes the catalyst to be more active and produce a higher olefin conversion. Additionally, clays heat treated in this manner are more stable, remaining active over longer periods during the oligomerization reaction. The clays may be heat treated at temperatures of 50 to 400°C, with or without the use of a vacuum. A more preferred temperature range is 50 to 300°C. Optionally, an inert gas may also be used during heat treatment. Preferably, the clay should be heat treated under conditions, and for a length of time, which will reduce the water content of the clay to 1 wt.% or less.

The oligomerization reaction may be carried out in either a stirred slurry reactor or in a fixed bed continuous flow reactor. The catalyst concentration should be sufficient to provide the desired catalytic effect. The temperatures at which the oligomerization may be performed are generally between 50 and 300°C, with the preferred range being from 150 to 180°C. The reaction may be run at pressures from ambient to 7 MPa (0 to 1000 psig).

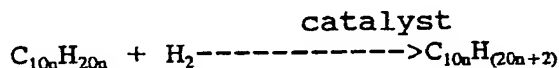
According to another embodiment of the present invention, we have surprisingly discovered that an even higher conversion of olefin into oligomer may be obtained when the acidic calcium montmorillonite clays are treated with a Lewis acid such as aluminium nitrate before they are used as a catalyst. Additionally, the resulting oligomer products contain a greater percentage of trimer and higher oligomers.

In the preferred form of this embodiment of the present invention, the clay is treated with aluminium nitrate before running the reaction. The clay can be added to a solution of 1 to 20 wt.%, preferably 10 wt.% of aluminium nitrate in water. The ratio of clay to aluminium nitrate solution should be sufficient to provide a washed and dried catalyst having a concentration of aluminium nitrate at least sufficient to give the Friedel-Crafts effect, preferably 0.01 to 10 wt.% of aluminium nitrate, but not so much that it inhibits the acid sites of the clay. The clay should remain in the aluminium nitrate solution under agitation for a period sufficient to meet these requirements.

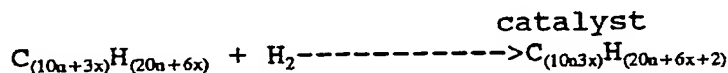
We have also found that advantageous results may be obtained when certain other Lewis Acid moderators are employed in the place of aluminium nitrate. For example, acidic montmorillonite clays treated with either nickel chloride or zinc chloride were found to yield a higher conversion of monomer into oligomer, and to produce an oligomer product having a better dimer/trimer ratio, than untreated acidic clays. Neither the nickel chloride-treated clay, nor the zinc chloride-treated clay, was capable, however, of achieving the conversion and dimer/trimer ratio obtained with the aluminium nitrate-treated clay, the preferred Lewis Acid treatment in the present invention. Other Lewis Acids may provide comparable results. However, clays treated with either of two other Lewis Acids, zirconium chloride and aluminium chloride, were found to produce a lower conversion of monomer to oligomer and/or a poorer dimer/trimer ratio than untreated clays.

Preferably, the aluminium nitrated-treated clay catalyst is heat-treated before running the reaction. The conditions used are generally the same as those disclosed above for the clays that have not been treated with Lewis acids.

Following the oligomerization reaction, the unsaturated oligomers may be hydrogenated to improve their thermal stability and to guard against oxidative degradation during their use as lubricants. The hydrogenation reaction for 1-decene oligomers may be represented as follows:

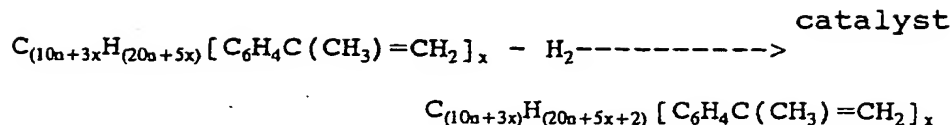


where n represents moles of monomer used to form the oligomer. Hydrogenation of propylene/1-decene co-oligomers may be represented as follows:



where n and x represent moles of long-chain alpha-olefin and propylene, respectively, used to form the co-oligomer.

Hydrogenation of 1,3-di-isopropenyl benzene/1-decene co-oligomers may be represented as follows:



where n and x represent moles of long-chain alpha-olefin and 1,3-di-isopropenyl benzene, respectively, used to form the co-oligomer.

Hydrogenation processes known to those skilled in the art may be used to hydrogenate the oligomers. A number of metal catalysts are suitable for promoting the hydrogenation reaction, including nickel, platinum, palladium, copper, and Raney nickel. These metals may be supported on a variety of porous materials such as kieselguhr, alumina, or charcoal. A particularly preferred catalyst for this hydrogenation is a nickel-copper-chromia catalyst described in US-A-3152998. Other known hydrogenation procedures are described in US-A-4045508, -4013736, -3997622 and -3997621.

If, in a continuous reaction, the recycle stream is not employed, it is desirable to strip any un-oligomerized monomer from the oligomer product.

While it is known to include a distillation step after the hydrogenation procedure to obtain products having various viscosities at 100°C, it is preferred in the method of the present invention that no further distillation (beyond monomer flashing) should be conducted. In other words, the monomer-stripped, hydrogenated bottoms are the desired synthetic lubricant components. Thus, the method of this invention does not require the costly, customary distillation step, yet, surprisingly, produces a synthetic lubricant component that has excellent properties and that performs in a superior fashion. In some instances, however, one skilled in the art may find subsequent distillation useful in the practice of this invention.

The monomer stripping step should be conducted under mild conditions. Distillation at temperatures exceeding 210°C may cause the oligomers to break down in some fashion and come off as volatiles. Preferably, therefore, the reboiler or pot temperature should be kept at or under 180°C when stripping out the monomer.

The invention will be further illustrated by the following Examples, which are given by way of illustration.

The following demonstrates the use of the present invention in batch reaction systems:

Batch-Flask

Olefin and clay catalyst were charged to a flask equipped with a stirrer, thermometer, heating mantle, and a water-cooled condenser (N₂ purge). The mixture was vigorously stirred and heated at a desired temperature for the desired time. The mixture was then cooled to ambient temperature and filtered with suction. The liquid was analyzed by liquid chromatography. The results are detailed in Table I.

Batch-Autoclave

Olefin and clay catalyst were charged to an autoclave. The autoclave was sealed and heated to the desired temperature for the desired time. The mixture was then cooled to ambient temperature and filtered with suction. The liquid was then analyzed by liquid chromatography. The results are shown in Table I.

Hydrogenation of Oligomer

An autoclave was charged with oligomer prepared in Batch No. 6 of Table I and finely powdered nickel catalyst. The autoclave was flushed with hydrogen and then pressurized to 7 MPa with hydrogen. The mixture was heated to 200°C and stirred at this temperature for 4 hours. The mixture was then repressurized with hydrogen to 13.89 MPa as needed. The mixture was then cooled to ambient temperature, the catalyst was filtered, and the monomer was removed. Typical results are shown in Table II.

TABLE 1

Batch No.	Olefin(s) (by carbon number)	(g)	Harshaw/ Filtrol	(g)	Reactor	Time/Temp (H)/(°C)	Con. (%)	M(%)	Results from LC		
									D(%)	T+(%)	D/T+ Ratio
1	C-14A	101	H/F Clay 13	25	Flask	3/150	81.9	18.1	49.1	32.8	1.50
2	C-14A	100	H/F Clay 24	25	Flask	4/150	92.4	7.6	43.9	48.4	0.91
3	C-14A	100	H/F Clay 13	10	Clave	4/300	78.9	21.1	55.3	23.4	2.36
4	C-14A	100	H/F Clay 24	10	Clave	4/300	57.6	42.4	46.4	11.2	4.14
5	C-14A	100	85% H ₃ PO ₄	10	Clave	4/300	15.6	84.4	7.87	7.69	1.02
6	C-14A	350	H/F Clay 24	50	Flask	4/150	80.0	20.0	49.0	31.0	1.58
7	C-131, 141 (40% 60%)	350	H/F Clay 24	50	Flask	4/150	63.5	36.5	45.7	17.7	2.58
8	C-131, 141C-14A	250	H/F Clay 24	50	Flask	4/150	67.1	32.9	48.7	18.4	2.65
9	C-131, 141 (40%, 60%)	350	H/F Clay 24	50	Flask	4/180	78.0	22.0	51.1	26.9	1.90
10	C-151, 161	350	H/F Clay 24	50	Flask	4/150	45.6	54.5	33.7	11.8	2.86
11	C-151, 161	350	H/F Clay 24	50	Flask	16/120	8.4	91.6	8.4	-0	-
12	C-14A, 16A (63%, 36%)	350	H/F Clay 24	50	Flask	3/150	78.6	21.4	48.6	30.0	1.62
13	C-14A, 16A (63% 36%)	400	H/F Clay 24	20	Flask	6/180	78.1	21.9	48.9	29.3	1.67
14	C-14A, 16A (63% 36%)	400	H/F Clay 24	10	Flask	7/180	63.5	36.5	48.7	24.8	1.96
15	C-14A, 16A (63% 36%)	400	H/F Clay 24	40	Flask	6/150	78.9	21.1	47.6	31.4	1.52

Con. = Conversion; M = Monomer; D = Dimer, T + = Trimer + Tetramer + etc.
A = Alpha; I = Internal

TABLE II
PROPERTIES OF HYDROGENATED OLIGOMER FROM BATCH NO. 6 (TABLE I)

5	Monomer	1.69 %
	Dimer	58.5 %
	Trimer	29.6 %
	Tetramer	9.53 %
	Pentamer	0.76 %
10	Pour Point (°C)	-34.5
	Viscosity	39.4 cSt (-4°C)
		24.4 cSt (38°C)
		4.69 cSt (99°C)
15	Viscosity Index	125
	% Remaining by Thermogravimetric Analysis	
	(233°C)	90.5 %
	(250°C)	83.5 %

20

EXAMPLE 2

The following tables demonstrate the use of the present invention in continuous reaction systems. The 100 cc reactor (see Table III) was a 74 x 1.6cm stainless steel tube. The catalyst bed was about 100 cc. Liquid feed was pumped through the bottom of the reactor with a Ruska pump. A Uni-flow valve and a Foxboro controller were used to regulate pressure. The reactor was electrically heated. The 300 cc reactor (see Table IV) was a 74 x 2.3cm stainless steel tube. The catalyst bed was about 300 cc. Other equipment was the same as described in connection with the 100 cc reactor.

The olefin was NEODENE 1518 IO of Shell Chemical Co., an internal olefin having the following constitution:-

	C ₁₄ and lower	1.8 %
35	C ₁₅	25.3 %
	C ₁₆	26.3 %
	C ₁₇	24.2 %
	C ₁₈	18.5 %
40	C ₁₉	3.9 %

45

50

55

TABLE III

Sample No.	Liquid Flow (CC)	Temp (C)	Reactor Press. (psig MPa)	Time Since Prior Sample (H)	C (%)	M (%)	D (%)	T+ (%)	D/T + Ratio
1	18	150	200/1.48	4	75.5	24.5	43.9	31.6	1.39
2	18	156	200/1.48	6	82.4	17.6	41.6	40.8	1.02
3	18	169	300/2.17	17	80.5	19.5	42.4	38.1	1.11
4	18	200	300/2.17	6	73.2	26.8	44.5	28.7	1.56
5	20	200	300/2.17	16	77.1	22.9	52.0	25.1	2.07
6	20	150	300/2.17	6	69.4	30.6	46.5	22.9	2.03
7	20	149	300/2.17	15	64.1	35.9	46.5	12.6	2.64
8	20	149	300/2.17	4	61.9	38.1	42.3	14.6	3.28
9	20	155	300/2.17	4	48.1	51.9	32.5	15.6	2.08
10	20	156	300/2.17	4	54.0	58.4	35.0	19.0	1.84
11	20	156	300/2.17	15	58.4	41.6	39.8	18.7	2.13
12	20	155	300/2.17	9	59.2	40.8	40.2	19.0	2.12
13	20	155	300/2.17	14	62.8	37.2	41.8	21.0	1.99
14	20	155	300/2.17	7	65.8	34.2	41.8	24.0	1.24
15	20	155	300/2.17	15	67.5	32.5	42.4	25.1	1.69
16	20	155	300/2.17	4	65.0	35.0	43.9	21.2	2.08
17	20	153	300/2.17	15	68.8	31.2	45.7	34.1	1.98

TABLE III

Sample No.	Liquid Flow (CC)	Temp (C)	Reactor Press. (psig MPa)	Time Since Prior Sample (H)	C (%)	M (%)	D (%)	T+ (%)	D/T + Ratio
18	20	156	300/2.17	9	73.7	26.3	48.3	25.4	1.90
19	20	156	300/2.17	15	77.2	22.8	47.4	29.8	1.59
20	20	156	300/2.17	15	77.2	22.8	47.4	29.8	1.59
21	20	156	300/2.17	16	72.3	22.7	49.3	28.0	1.76
22	20	156	300/2.17	24	74.4	25.6	48.6	25.8	1.89
23	20	156	300/2.17	8	72.4	27.6	49.6	22.8	2.18
24	20	156	300/2.17	16	71.1	8.9	48.0	23.2	2.07
25	20	156	300/2.17	24	68.1	31.9	32.3	20.7	2.28
26	20	158	300/2.17	9	66.4	33.6	46.8	19.6	2.39
27	20	156	300/2.17	24	66.5	33.3	46.2	20.3	2.27
28	20	156	300/2.17	15	64.1	35.9	46.4	12.9	2.62
29	20	156	300/2.17	9	64.1	39.9	44.1	20.0	2.21
30	20	156	300/2.17	15	62.4	37.6	48.1	18.4	2.40
31	20	156	300/2.17	9	-	-	-	-	-
32	20	156	300/2.17	15	-	-	-	-	-
33	20	155	300/2.17	9	57.9	42.1	41.8	16.7	2.46
34	20	154	154/1.16	15	56.6	43.4	42.2	16.4	2.93

Distillation of Oligomers Prepared from C-12 Alpha-Olefin

Fractions from a C₁₂ run described in Table III were combined to give 1741 grams of product, which had the following analysis by liquid chromatography:

Monomer 27.8 %

EP 0 449 453 A2

Dimer 48.0 %
 Trimer 19.3 %
 Tetramer 4.91%

- 5 This material was vacuum distilled through a 25cm Goodloe packed column until a pot temperature of 236°C was reached. Four fractions were collected. The fourth fraction, boiling point 165 - 170°C, at 1.1KPa, was 93.4% C₁₂ dimer. The pot residue was free of dimer and monomer. The reduced stripped dimer had the following properties:

10

Viscosity 99°C 2.50 cSt
 Viscosity Index 78.5
 Pour Point °C <-45.5

15

% Remaining by TGA
 233°C 30%
 250°C 1%

- 20 The reduced pot residue had the following properties:

Viscosity (99°C) 8.40 cSt
 Viscosity Index 128
 Pour Point (°C) -29

25

% Remaining by TGA
 233°C 99%
 250°C 98%

30

35

40

45

50

55

TABLE IV

Sample No.	Liquid Flow (CC)	Temp (C)	Reactor Press. (psig MPa)	Time Since Prior Sample (H)	C (%)	M (%)	D (%)	T+ (%)	D/T + Ratio
1	48	150/155	300/2.17	3	5.4	94.5	5.1	0.4	12.8
2	48	151/158	300/3.17	15	32.4	67.6	24.0	8.4	2.86
3	48	151/158	300/2.17	4	64.3	35.7	39.3	25.0	1.57
4	48	151/157	300/2.17	5	59.1	40.9	44.4	14.7	3.02
5	48	152/157	300/2.17	15	58.6	41.4	44.6	14.1	3.16
6	48	148/153	300/2.17	25	64.4	35.6	47.6	16.7	2.85
7	48	149/155	300/2.17	8	68.1	32.0	43.9	19.4	2.26
8	48	146/154	300/2.17	15	65.2	34.8	48.3	16.9	2.86
9	48	148/152	300/2.17	9	68.6	31.5	45.1	23.4	1.93
10	48	143/152	300/2.17	4	62.4	37.6	42.7	19.8	2.16
11	48	143/152	300/2.17	19	62.0	38.0	43.1	19.0	2.27
12	48	141/150	300/2.17	5	61.5	38.5	43.6	17.9	2.44
13	48	141/150	300/2.17	4	63.1	36.9	43.9	19.2	2.29
14	48	143/152	300/2.17	15	62.7	37.3	43.5	19.1	2.28
15	48	145/153	300/2.17	9	60.1	39.9	46.7	23.4	2.00
16	48	147/157	300/2.17	16	59.2	40.8	45.2	14.0	3.23
17	48	147/156	300/2.17	8	63.4	36.6	44.6	18.8	2.37
18	48	147/156	300/2.17	15	60.2	39.9	46.6	13.5	3.45

TABLE IV

Sample No.	Liquid Flow (CC)	Temp (C)	Reactor Press. (psig MPa)	Time Since Prior Sample (H)	C(%)	M(%)	D(%)	T+(%)	D/T + Ratio
19	48	151/159	300/2.17	9	59.2	40.8	46.1	13.1	3.52
20	48	151/159	300/2.17	15	55.4	44.6	44.1	11.4	3.89
21	48	151/159	300/2.17	3	56.3	43.7	39.9	16.2	2.46
22	48	141/155	300/2.17	15	47.7	52.3	38.7	8.96	4.32
23	48	145/155	300/2.17	9	48.0	52.0	39.0	9.00	4.33
24	48	145/155	300/2.17	15	43.9	56.1	35.2	8.69	4.05
25	48	147/156	300/2.17	9	39.7	60.4	32.5	2.13	4.56
26	48	147/156	300/2.17	15	41.0	59.0	33.3	2.32	4.31
27	48	139/155	300/2.17	4	25.6	24.4	20.7	4.93	4.20
28	48	145/155	300/2.17	15	39.5	60.5	31.0	8.43	3.68
29	48	146/155	300/2.17	4	35.9	64.1	30.2	5.74	5.26
30	48	146/155	300/2.17	17	32.2	67.8	26.8	5.43	4.94
31	48	146/155	300/2.17	9	29.9	70.1	24.3	5.64	4.31
32	56	146/155	300/2.17	15	28.0	72.0	23.5	4.59	5.12
33	50	148/158	300/2.17	9	26.0	74.0	21.8	4.22	5.17
34	50	148/158	300/2.17	15	27.6	78.4	23.1	4.55	5.08
35	50	148/158	300/2.17	9	28.8	71.2	23.7	5.09	4.66

Distillation of Oligomers Prepared from Neodene 1518 IO

Samples 2, 5, 6, 7, and 8 from Table IV were combined to yield a total of 2600 grams of material, which had the following analysis by liquid chromatography:

Monomer 37.8 %

Drimer 40.2 %
Trimer 17.8 %
Tetramer 4.08%

5 The material was placed in a five-liter flask and distilled through a 25cm Goodloe packed column until a pot temperature of 270 °C was reached (1.1 kPa). The pot residue (976 grams) was reduced with hydrogen and a nickel catalyst (5 wt.% catalyst, 200 °C, 4.0 hours 13.9 MPa hydrogen). The material obtained after filtration had the following properties:

10	Viscosity (99°C)	8.40 cSt
	Viscosity Index	128
	% Remaining by TGA	
	233°C	99 %
15	250°C	98 %

EXAMPLE 3

20 This example demonstrates the superior results obtained when the clay catalysts are heat treated before oligomerizing the olefin.

Filtrol Clay-124 (200 grams) was placed in a vacuum and heat treated overnight for 20 hours at approximately 160 °C and a pressure of approximately 2.67 kPa. Before being heat treated, the clay had a moisture content of 7.11 wt.%. After being heat treated, the moisture content was 1.03 wt.%. Results
25 obtained when the heat treated clay was used to catalyze the oligomerization of C₁₄ alpha-olefin are shown in Table V, below. Table VI, showing the results when the clay is not heat treated, is offered for comparison.

30

35

40

45

50

55

TABLE V

Sample No.	Liquid Flow (CC)	Temp (C)	Reactor Press. (psig MPa)	Time Since Prior Sample (H)	Total Time	C(%)	M(%)	D(%)	T+(%)	D/T Ratio
1	16	153	300	63	(63)	76.0	24.0	50.1	25.9	1.93
2	16	155	300	9	(72)	44.0	56.0	32.1	11.9	2.70
3	16	155	300	15	(87)	80.4	19.6	50.0	29.8	1.69
4	19	155	300	9	(96)	80.1	19.9	50.7	29.3	1.73
5	19	156	300	15	(11)	80.3	19.7	51.3	29.0	1.77
6	19	156	300	9	(120)	82.1	17.9	42.4	34.8	1.36
7	19	156	300	15	(135)	81.6	18.4	48.1	33.4	1.44
8	19	156	300	8	(143)	81.6	18.4	49.2	32.4	1.52
9	19	156	300	16	(159)	81.1	18.9	49.8	31.3	1.59
10	19	156	300	9	(168)	80.2	19.8	49.2	31.0	1.59
11	19	156	300	63	(231)	81.2	18.8	49.9	31.2	1.60
12	19	156	300	9	(240)	79.9	20.3	52.5	27.2	1.93
13	19	156	300	15	(255)	78.4	21.6	55.9	22.4	2.49
14	19	156	300	9	(264)	78.0	22.0	55.8	22.2	2.51
15	16	156	300	15	(279)	79.0	21.0	58.2	25.8	2.06
16	16	156	300	9	(288)	72.5	22.5	56.1	21.5	2.61
17	20	156	300	15	(303)	79.0	21.0	51.6	22.4	1.88

TABLE V

Sample No.	Liquid Flow (CC)	Temp (C)	Reactor Press. (psig MPa)	Time Since Prior Sample (H)	Total Time	C (%)	M (%)	D (%)	T+ (%)	D/T Ratio
18	20	156	300	9	(312)	72.9	22.1	52.3	25.8	2.03
19	20	156	300	15	(327)	76.9	23.1	52.4	24.5	2.14
20	20	156	300	9	(336)	75.5	24.5	52.2	23.3	2.24
21	20	156	300	63	(399)	73.5	26.4	51.9	21.7	2.39
22	20	156		9	(408)	68.7	31.1	51.0	17.7	2.88

TABLE VI

Sample No.	Liquid Flow (CC)	Temp (C)	Reactor Press. (psig MPa)	Time Since Prior Sample (H)	Total Time	C(%)	M(%)	D(%)	T+(%)	D/T Ratio
1	20	155	300	8	8	73.5	26.5	47.1	26.3	1.75
2	20	155	300	14	14	77.1	22.9	46.8	30.5	1.53
3	20	155	300	14	30	77.3	22.7	48.0	28.3	1.71
4	20	155	300	16	46	78.8	21.1	48.1	29.6	1.63
5	20	155	300	8	54	79.8	20.2	48.3	31.5	1.53
6	20	155	300	15	69	79.9	20.1	47.1	32.8	1.44
7	20	155	300	9	78	79.6	20.4	47.6	32.0	1.49
8	20	155	300	63	141	78.2	21.3	49.9	28.5	1.75
9	20	155	300	9	150	77.2	22.8	51.2	26.1	1.96
10	20	155	300	15	165	75.9	24.2	51.6	24.2	2.13
11	20	156	300	9	174	73.7	26.3	52.7	21.0	2.15
12	20	156	300	15	189	78.9	27.1	50.0	22.9	2.18
13	20	156	300	9	198	72.8	27.7	49.9	22.4	2.23
14	20	156	300	15	213	71.7	28.3	49.9	22.2	2.25
15	20	156	300	9	222	70.5	29.5	50.3	20.2	2.49
16	20	154	300	15	232	70.1	29.9	49.9	20.2	2.47
17	24	155	300	7	244	62.2	32.8	47.3	19.9	2.38
18	24	155	300	65	309	62.2	37.7	45.5	16.8	2.71
19	24	155	300	90	318	59.1	40.9	43.9	15.2	2.89
20	24	155	300	15	333	56.8	43.2	44.0	22.7	1.94

TABLE VI

Sample No.	Liquid Flow (CC)	Temp (C)	Reactor Press. (psig MPa)	Time Since Prior Sample (H)	Total Time	C(%)	M(%)	D(%)	T+(%)	D/T Ratio
21	24	155	300	9	342	56.5	43.5	41.8	14.7	2.84
22	24	155	300	15	357	54.1	45.9	42.5	11.6	2.66
23	24	155	300	9	366	52.0	48.0	40.7	11.2	3.57
24	24	155	300	15	381	50.7	49.3	40.1	10.6	3.78
25	24	155	300	9	390	49.6	50.4	38.1	11.5	3.31
26	24	155	300	15	405	50.2	49.8	32.9	12.4	3.06
27	24	155	300	9	414	47.3	52.7	37.8	9.47	3.99
28	24	154	300	63	417	48.2	51.8	32.8	10.4	3.63
29	24	155	300	9	486	51.4	48.6	34.6	7.17	4.83
30	24	155	300	15	501	49.4	50.6	37.1	12.3	3.02
31	19	155	300	9	510	45.8	54.2	36.7	9.10	4.03
32	20	155	300	15	525	45.5	54.4	36.1	9.38	3.85
33	20	155	300	9	534	44.9	55.1	35.6	8.21	4.47
34	20	155	300	15	549	43.5	56.3	36.7	7.89	4.51
35	20	155	300	8	557	42.3	57.7	34.3	7.94	4.32
36	19	155	300	16	573	41.4	58.6	34.2	7.28	4.65
37	19	155	300	9	582	39.2	60.8	32.4	6.80	4.76
38	19	155	300	63	645	38.7	61.3	31.8	6.93	4.59
39	19	155	300	9	654	44.1	55.9	35.5	8.57	4.14
40	19	155	300	15	661	37.5	62.5	30.7	6.75	4.55

In Tables V and VI above, conversion of C₁₄ alpha-olefin against time is shown for heat treated Harshaw/Filtrol Clay 124 (1.0 wt.% H₂O) and non-heat treated clay 124 (7.1 wt.% H₂O), respectively. The reaction conditions for both continuous reactions were 155° C, and 2.17 MPa, with an LHSV (Liquid Hourly Space Velocity) of 0.2. Table V demonstrates the increased activity and prolonged catalyst life achieved by heat treating the clay before its use as a catalyst, showing 80 to 82% conversion at 90 to 230 hours, and 72 to 79% conversion from 250 to 400 hours, total continuous reaction time. Table VI, on the other hand,

shows that the non-heat treated clay was less active at peak activity (achieving 70 to 79% conversion), and that its activity decreased more rapidly (conversion dropped to 62% and then to below 50% by 400 hours, total continuous reaction time.)

5 The embodiment of the invention using mixtures of linear olefins will be illustrated by the following Examples 4 to 11, in which the following procedures were used:

Batch-Flask

10 Olefin and clay catalyst were charged to a flask equipped with a stirrer, thermometer, heating mantle, and a water-cooled condenser (N₂ purge). The mixture was vigorously stirred and heated at a desired temperature for the desired time. The mixture was then cooled to ambient temperature and filtered with suction. The liquid was analyzed by liquid chromatography. The results are detailed in Tables VII and IX.

Batch-Autoclave

15 Olefin and clay catalyst were charged to an autoclave. The autoclave was sealed and heated to the desired temperature for the desired time. The mixture was then cooled to ambient temperature and filtered with suction. The liquid was then analyzed by liquid chromatography. The results are shown in Table VII and IX.

Hydrogenation of Oligomer

20 An autoclave was charged with oligomer and finely powdered nickel catalyst. The autoclave was flushed with hydrogen and then pressurized to 7.0 MPa with hydrogen. The mixture was heated to 200 °C and stirred at this temperature for 4 hours. The mixture was then repressurized with hydrogen to 13.9 MPa as needed. The mixture was then cooled to ambient temperature, the catalyst was filtered and the monomer was removed. The results are shown in Tables VIII and X.

30

35

40

45

50

55

TABLE VII

EXAMPLE NO.	OLEFIN	(g)	HARSHAW/FILTROL CATALYST	(g)	REACTOR	TIME TEMP (H) (°C)	CON. M (%)	D (%)	T+ (%)	D/T+ RATIO
4	C-14A, 16A (63%, 36%)	400	H/F Clay 113	40	Clave	4 180°	84.8	15.2	49.9	34.9 1.43
5	C-14A, 16A C-16I	200	H/F Clay 24	40	Flask	6 150	71.1	28.9	48.1	23.0 2.09
6	C-14A, 16A C-16I	200	H/F Clay 24	40	Clave	4 180	80.1	19.9	50.8	29.3 1.73
7	C-14A, 16A C-16I	300	H/F Clay 24	40	Clave	4 180	78.2	21.8	52.5	25.8 2.03

Con. = Conversion; M = Monomer; D = Dimer; T+ = Trimer, plus Tetramer, Pentamer, etc.
 A = Alpha; I = Interest

TABLE VIII

PROPERTIES OF REDUCED OILGOMER BOTTOMS

EXAMPLE NO.	Percent Remaining by TGA at 121°C	Viscosity at (cst) 99°C	VI	Pour Point °C
4	89.5	6.17	131	-29
5	87.7	5.21	135	-32
6	92.5	5.79	129	-37
7	87.5	5.68	130	-37

TGA = Thermogravimetric Analysis
VI = Viscosity Index

TABLE IX

ACID CLAY CATALYZED OLEFIN OLIGOMERIZATION USING RECYCLE OLEFIN

EXAMPLE NO.	OLEFIN	(g) CATALYST	(g) REACTOR	TIME TEMP (H) (°C)	CON. M (%)	D (%)	T+ (%)	D/T+ RATIO
8	14A	400 H/F Clay-124	40 Clave	5	160 78.3	21.7	48.8	29.5 1.65
9	14A 14-recycle	300 H/F 100 Clay-124	40 Clave	5	160 74.6	25.4	47.2	27.5 1.72
10	14A 14-recycle	300 H/F 100 Clay-124	40 Flask	5	160 73.7	25.3	48.5	26.2 1.85
11	14A 14-recycle	300 H/F 100 Clay-124	40 Flask	5	160 74.9	25.1	45.2	29.7 1.52

TABLE X

PROPERTIES OF REDUCED OLIGOMER BOTTOMS

EXAMPLE NO.	wt.% Recycle	Percent Remaining by TGA 121°C	Viscosity (cSt)	VI	Pour Point °C
8	0	88.5	6.61	121	-29
9	25	85.9	5.14	127	-34
10	25	83.0	5.09	127	-37
11	25	80.5	4.99	126	-37

Examples 12 to 16 detailed in Table IX below demonstrate the embodiment of the present invention in which C₁₀₋₂₄ linear olefins and propylene are co-oligomerized in batch reaction systems:

Co-oligomerization Procedure

1-Tetradecene (90 g) and catalyst (10 g Harshaw/Filtrol Clay grade 24) were charged to a 1 litre autoclave, and the autoclave was sealed. Propylene was pressurized in and the mixture was heated at 160°C for five hours. The pressure dropped slowly during the run as propylene was reacted. At the end of the run, the mixture was cooled to ambient temperature, a small amount of propylene was vented, and the mixture was filtered with suction. Analysis of the reaction mixture by high pressure liquid chromatography showed the presence of dimers, trimers, and higher oligomers. Percentage conversions obtained and dimer/trimer ratios are shown in Table XI.

Hydrogenation of Co-oligomers

An autoclave was charged with finely powered nickel catalyst and co-oligomer prepared according to the procedure outlined above. The autoclave was flushed with hydrogen and then pressurized to 7 MPa with hydrogen. The mixture was heated to 200°C and stirred at this temperature for 4 hours. The mixture was repressurized with hydrogen to 13.9 MPa as needed. The mixture was then cooled to ambient temperature, the catalyst was filtered and the monomer was removed. Properties of the reduced co-oligomers are recorded in Table XI below.

TABLE XI

CO-OLIGOMERIZATION OF PROPYLENE AND 1-TETRADECENE USING H/F CLAY-24

EX. NO.	PROPYLENE (% BY WT. OF OLEFIN MIXTURE)	% CON OF C ₁₄ ALPHA-OLEFIN	D/T+ RATIO	TGA-% REMAINING AT 250°C	VIS AT 99°C (Cst)	VI	POUR POINT (°C)
12	5 (5 g)	-	-	85.0	5.13	133	-37
13	10 (10 g)	61.6	2.87	79.0	4.67	123	-40
14	15 (15 g)	52.4	4.50	81.5	4.68	122	-37
15	20 (20 g)	43.8	6.02	84.3	4.44	115	-40
16	0	78.3	1.65	88.5	6.61	121	-29

Con. = Conversion; D = Dimer; T+ = Trimer, plus Tetramer, Pentamer, etc; TGA = Thermogravimetric Analysis; Vis. = Viscosity; and VI = Viscosity Index.

Properties were determined on reduced bottoms.

Examples 17 to 23 detailed in Table XII below demonstrate the embodiment of the present invention in which 1,3-diisopropenyl benzene or alpha-methylstyrene are used in batch reaction systems:

Co-oligomerization Procedure

Reactants and catalyst (10 wt.%, Harshaw/Filtrol Clay 124) were charged to a three-necked flask equipped with an overhead stirrer, a water cooled condenser, a heating mantle and a nitrogen purge. The mixture was heated to the desired temperature for the desired period of time (with vigorous stirring.) At the end of the reaction, the mixture was cooled to ambient temperature and filtered with suction. Analysis of the

reaction mixture by high pressure liquid chromatography showed the presence of dimers, trimers, and higher oligomers. Percent conversions and dimer/trimer ratios are shown in the table below.

Hydrogenation of Co-oligomers

5

An autoclave was charged with finely powdered nickel catalyst (5 wt.%) and co-oligomer prepared according to the procedure outlined above. The autoclave was flushed with hydrogen and then pressurized to 7 MPa with hydrogen. The mixture was heated to 200 °C and stirred at this temperature for 4 hours. The mixture was repressurized with hydrogen to 13.9 MPa as needed. The mixture was then cooled to ambient
10 temperature, the catalyst was filtered and the monomer was removed under vacuum (approx. 130 Pa). Properties of the reduced co-oligomers are recorded in Table XII below.

15

20

25

30

35

40

45

50

55

TABLE XII
CO-OLIGOMERIZATION OF 1,3-DI-ISOPROPENYL BENZENE AND 1-TETRADENCENE USING H/F CLAY-124

EX. NO.	OLEFIN FEED	% BY WT. OF OLEFIN MIXTURE	CATALYST	% CON. OF C ₁₄ ALPHA-OLEFIN	D/T+ RATIO	TGA - % REMAINING AT 250°C	Vis. AT 99°C (cst)	VI	POUR POINT °C
17	C-14A 1,3-DIPB	90 10	Clay-124	66.2	1.66	92.6	8.62	112	-37
18	C-14A 1,3-DIPB	95 5	Clay-124	73.5	1.41	86.5	6.35	119	-34
19	C-14A 1,3-DIPB	90 10	Heat-Treated Clay-124	36.3	3.37	90.0	11.9	101	-32
20	C-14A 1,3-DIPB	95 5	Heat-Treated Clay-124	50.2	2.92	86.5	6.63	119	-37
21	C-14A AMS	95 5	Clay-124	75.1	1.90	87.1	5.66	132	-37
22	C-14A	95	Heat-	67.8	1.85	82.8	5.84	119	-32
23	C-14A	100	Clay-124	78.3	1.65	88.5	6.61	121	-29

Con. = Conversion; D = Dimer; T+ = Trimer, plus Tetramer, Pentamer, etc; TGA = Thermogravimetric Analysis; Vis. = Viscosity Index; A = Alpha; 1,3-DIPB = 1,3-Di-isopropenyl benzene; and AMS = Alpha Methyl Styrene.

Examples 24 to 31 detailed in Table XIII below demonstrate the embodiment of the present invention in which linear and vinylidene olefins are co-oligomerized in batch reaction systems:

Procedure

Olefin and Harshaw/Filtrol Clay-13 catalyst (40 g) were charged to a flask equipped with a stirrer, thermometer, heating mantle, and a water-cooled condenser (N₂ purge). The mixture was vigorously stirred and heated at a desired temperature for the desired time. The mixture was then cooled to ambient temperature and filtered with suction. The liquid was analyzed by liquid chromatography. Olefin conversion and dimer/trimer ratio were determined and are detailed in the table below.

Hydrogenation of Oligomer

An autoclave was charged with oligomer and finely powdered nickel catalyst. The autoclave was flushed with hydrogen and then pressurized to 7 MPa with hydrogen. The mixture was heated to 200 °C and stirred at this temperature for 4 hours. The mixture was repressurized with hydrogen to 13.9 MPa as needed. The mixture was then cooled to ambient temperature, the catalyst was filtered and unreacted monomer was removed. Properties of the resulting synthetic lubricant base stocks are shown in Table XIII below.

TABLE XIII
CO-OLIGOMERIZATION OF VINYLIDENE OLEFIN AND ALPHA- OR INTERNAL-OLEFIN¹

EX. NO.	OLEFIN	(g) OF OLEFIN	WT. % OLEFIN AS VINYLIDENE	TIME/TEMP (Hr)/(°C) OF	CON. (%)	D/T+ RATIO	Properties After Hydrogenation			
							VIS. 089°C INDEX	NOACK (%)	CCSIM (cp)	POUR POINT
24	1416 ¹	400	20	5/160	81.4	1.58	5.43	13.7	800	-29
25	1416	400	20	2/160	82.3	1.60	5.59	14.3	855	-32
				2/180						
26	1416	400	<5	5/160	85.0	1.28	6.08	12.0	880	-23
27	1416	400	<5	2/160	84.0	1.13	6.04	10.0	1015	-21
				2/180						
28	16 ²	400	<5	2/160	84.0	1.32	7.17	8.3	1550	-9
29	16 / 380/	20	5	2/160	81.1	1.64	6.46	7.4	1077	-15
	14-vin			2/180						
30	16 / 360/	10	10	2/160	91.6	0.79	5.92	8.4	888	-18
	14-vin	40		2/180						
31	1518I ³ /	320/	20	5/160	42.6	4.67	5.53	*	*	-29
	14-vin	80								

Vin. = vinylidene; Con. = conversion; I = Internal; Vis. = Viscosity; * = not determined; D = Dimer; T+ = Trimer + Tetramer + Pentamer, etc.; CCSIM = cold crank simulation; and cp = centipoise.

¹ From Ethyl Corporation: 1.3% C₁₂; 64.7% C₁₄; 33.0% C₁₆; and 1.0% C₁₈; containing approx. 19% of total olefin in vinylidene form.

² From Shell Chemical Co.: approx. 55% C₁₄ and 45% C₁₆; containing approx. 94.9% in alpha form and less than 5% in vinylidene form.

³ Shell Chemical Co. Neodene 1518 Internal Olefin: 1.8% C₁₄ and lower; 25.3% C₁₆; 26.3% C₁₈; 24.2% C₁₇; 18.5% C₁₉; and 3.9% C₂₀.

⁴ The catalyst for each of examples 24 to 31 was Harshaw/Filtrol Clay-13 (40g).

Example 32

The following Example 32 demonstrates the use of the present invention in continuous reaction systems. A 500 cc stainless steel reactor was charged with Harshaw/Filtrol Clay-24 and then heated for three days with a nitrogen purge (to drive off H₂O). The reactor was cooled to reaction temperature (155° C)

and a 1416 α olefin mixture containing 20% of vinylidene olefin (determined by NMR) was pumped through the catalyst bed at a rate of 80 g/hour.

Initially, the reactor effluent showed 77.7% conversion and a dimer/trimer+ ratio of 1.44. After four weeks, the conversion had dropped to 37.5%. Monomer was distilled off to give 23 litres of material. The

5 "bottoms" product was reduced with nickel catalyst to give a lubricant with the following properties:

Viscosity (99 °C) 5.32 cSt

Viscosity Index 120

Pour Point (°C) -46

CCSIM (-20 °C) 859 cp

10 Noack (250 °C) 14.4%

The embodiment of the invention in which a Lewis acid is deposited on the catalyst will be illustrated by the following Examples, 33 to 45, detailed below in Table XIV in which the following procedures were used:

Aluminium Nitrate Treatment

15

To 100 cc of Harshaw/Filtrol Grade 24 granules was added 1 litre of 0.5 N aqueous aluminium nitrate solution. The mixture was stirred mechanically for two days at room temperature. The solids were then filtered off and washed with distilled water until aluminium ions could no longer be detected in the washings. The remaining solids were then dried under a vacuum at 40 °C. 108 g of white solid were recovered.

20 Analysis showed the presence of 5.9% aluminium

Other Lewis Acid Treatments

100 cc samples of Harshaw/Filtrol Grade 24 granules were also treated, using the procedure detailed
25 above, with aqueous solutions of the following Lewis Acids:

	<u>Lewis Acid</u>	<u>Analysis of Treated Clay</u>
30	AlCl ₃	Al, 6.5 %
	ZrCl ₄	Zr, 3.8 %
	NiCl ₂	Ni, 0.2 %
	ZnCl ₂	Zn, 1.3 %
35	TiCl ₄	Ti, 5.1 %

Batch Oligomerizations

40

Olefin and clay catalyst were charged to a flask equipped with a stirrer, thermometer, heating mantle, and a water-cooled condenser (N₂ purge). The mixture was vigorously stirred and heated to a desired temperature for the desired time. The mixture was then cooled to ambient temperature and filtered with suction.

45 The liquid was analyzed by liquid chromatography. The results are detailed in Table XIV.

50

55

TABLE XIV

OLEFIN OLIGOMERIZATION USING ACIDIC CLAYS TREATED WITH ALUMINIUM NITRATE AND OTHER LEWIS ACIDS

EX. NO.	OLEFIN	(g)	CATALYST ¹	(g)	TIME (H.)	TEMP. (°C)	CON. (%)	M (%)	D (%)	T+ (%)	D/T+ RATIO
33	C-14A	100	H/F Clay-24	10.0	5.0	160	81.0	19.0	48.7	32.3	1.51
34	C-14A	100	Al(NO ₃) ₃ on H/F-24	10.0	5.0	160	85.0	15.0	45.2	39.8	1.14
35	C-14A	100	Al(NO ₃) ₃ on H/F-24	5.0	5.0	160	75.0	25.0	46.9	27.1	1.73
36	C-14A	100	H/F Clay-24	10.0	6.0	150	76.8	23.2	47.0	29.1	1.62
37	C-14A	100	Al(NO ₃) ₃ on H/F-24	10.0	6.0	150	80.2	19.8	47.5	32.8	1.45
38	C-14A	100	Al(NO ₃) ₃ on H/F-24	10.0	4.0	180	82.3	17.7	50.8	31.5	1.61
39	C-14A	100	H/F Clay-24	10.0	5.0	160	78.3	21.7	46.8	31.5	1.49
40	C-1518-10 ¹ 100	100	H/F Clay-24	10.0	5.0	180	67.4	32.6	47.3	19.1	2.48
41	C-1518-10	100	Al(NO ₃) ₃ on H/F-24	10.0	4.0	180	70.5	29.5	48.7	21.8	2.23
42	C-14A	100	NiCl ₂ on H/F-24	10.0	5.0	160	82.3	17.7	45.9	36.4	1.26
43	C-14A	100	ZnCl ₂ on H/F-24	10.0	5.0	160	83.2	16.8	43.1	37.6	1.15
44	C-14A	100	ZnCl ₄ on H/F-24	10.0	5.0	160	69.8	30.2	40.0	29.8	1.34
45	C-14	100	AlCl ₃ on HF-24	10.0	5.0	160	80.3	19.7	48.4	31.9	1.52

Con.=Conversion; M = Monomer; D = Dimer; T+ = Trimer, plus Tetramer, Pentamer etc.
A = Alpha

¹Shell Chemical Co. Neodene ^(a) 1518 Internal Olefin: 1.8% C₁₄ and lower; 25.3% C₁₅; 26.3% C₁₆; 24.2% C₁₇; 18.5% C₁₈; and 3.9% C₁₉.

55 Claims

1. A process for the preparation of oligomers or co-oligomers of linear olefins containing from 10 to 24 carbon atoms in which an olefin composition comprising said olefins is contacted with a catalyst,

characterized in that the catalyst is an acidic calcium montmorillonite clay having a moisture content up to 20 wt.%, a residual acidity of up to 30 mg KOH/g, and a surface area of 300 M²/g or greater.

2. A process according to Claim 1 characterized in that the linear olefins comprise alpha-olefins, internal olefins, or a mixture thereof.
3. A process according to Claim 1 or 2 characterized in that the olefin composition comprises said linear olefins and up to 20 weight % of propylene.
4. A process according to Claim 1 or 2 characterized in that the olefin composition comprises said linear olefins and up to 20 weight % of 1,3-di-isopropenyl benzene or alpha-methylstyrene.
5. A process according to Claim 1 or 2 characterized in that the olefin composition comprises said linear olefins and a vinylidene olefin having 10 to 24 carbon atoms.
6. A process according to Claim 5 characterized in that the olefin composition contains 5 to 40 weight % of the vinylidene olefin.
7. A process according to any one of Claims 1 to 6 characterized in that the clay is one on which at least 0.01 wt % of a Lewis Acid selected from aluminium nitrate, zinc chloride, and nickel chloride has been deposited.
8. A process according to Claim 7 characterized in that 0.01 to 10 wt % of aluminium nitrate is deposited on the clay.
9. A process according to any one of Claims 1 to 8 characterized in that the olefin composition is contacted with the clay at a temperature of 150 to 180 °C.
10. A process according to any one of Claims 1 to 9 characterized in that the oligomerized product is hydrogenated.

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 449 453 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 91302130.9

(51) Int. Cl.⁵: **C07C 2/08, C07C 2/24,
C07C 2/22**

(22) Date of filing: 13.03.91

(30) Priority: 28.03.90 US 500631
14.05.90 US 522941
21.05.90 US 525807
30.04.90 US 516931
04.09.90 US 577385
30.04.90 US 516870

(43) Date of publication of application:
02.10.91 Bulletin 91/40

(84) Designated Contracting States:
BE DE FR GB IT

(88) Date of deferred publication of the search report:
27.11.91 Bulletin 91/48

(71) Applicant: **TEXACO CHEMICAL COMPANY**
3040 Post Oak Boulevard
Houston, Texas 77056(US)

(72) Inventor: Marquis, Edward Thomas
9004 Colinfeld Drive
Austin, Texas 78758(US)
Inventor: Sanderson, John Ronald
P O Box 587
Leander, Texas 78641(US)
Inventor: Knifton, John Frederick
P O Box 15730
Austin, Texas 78726(US)

(74) Representative: **Brock, Peter William et al**
URQUHART-DYKES & LORD 91 Wimpole
Street
London W1M 8AH(GB)

(54) **Process for oligomerizing olefins to prepare base stocks for synthetic lubricants.**

(57) Linear olefins having 10 to 24 carbon atoms can be oligomerized to form synthetic lubricant base stocks by means of acidic calcium montmorillonite clay having a moisture content up to 20 wt%, a residual acidity of up to 30 mg KOH/g, and a surface area of 300 M²/g or greater. In a preferred embodiment, a Lewis acid such as aluminium nitrate is deposited on the clay.

The linear olefins can be alpha olefins, internal olefins or mixtures thereof, or the linear olefins can be co-oligomerized with propylene, with 1,3-dihisopropenylbenzene or alpha-methylstyrene, or with vinylidene olefins.

The oligomers are preferably hydrogenated to improve their stability.

EP 0 449 453 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 2130

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GB-A-1 489 646 (GULF RESEARCH AND DEVELOPMENT CO.) * Example 1 * -----		C 07 C 2/08 C 07 C 2/24 C 07 C 2/22
A,D	US-A-4 531 014 (GREGORY et al.) -----		
A	US-A-1 938 945 (C.R. WAGNER) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 07 C 2/00
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 17 September 91	Examiner VAN GEYT J.J.A.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document</div>			